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Diffusion through Carbon Nanotube Semipermeable membranes

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Auspices Statement

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FY05 LDRD Final Report
Diffusion through Carbon Nanotube Semipermeable membranes
LDRD Project Tracking Code: 03-ERD-050
Olgica Bakajin, Principal Investigator

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3) "Fabrication of a Carbon Nanotube-Embedded Silicon Nitride Membrane for Studies of Nanometer-Scale Mass Transport", J. Holt, A. Noy, T. Huser, D. Eaglesham, and O. Bakajin, *Nanoletters* 4(11), 2245-2250 (2004);

3) "Carbon Nanotube-Based Membranes: A Platform for Studying Nanofluidics", Jason K. Holt, Hyung Gyu Park, Olgica Bakajin, Aleksandr Noy, Thomas Huser, and David Eaglesham, IEEE Nanotech 2004 Symp. Proc.; Munich, Germany, 2004.

4) "Carbon Nanotube Based Permeable Membranes", J. Holt, H. Park, O. Bakajin, A. Noy, T. Huser, and D. Eaglesham Mat. Res. Soc. Symp. Proc., Vol 820, O4.3, 2004.

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PROJECT GOAL, SCOPE, SCIENCE AND TECHNOLOGY IMPACT

The goal of this project is to measure transport through CNTs and study effects of confinement at molecular scale. This work is motivated by several simulation papers in high profile journals that predict significantly higher transport rates of gases and liquids through carbon nanotubes as compared with similarly-sized nanomaterials (e.g. zeolites). The predictions are based on the effects of confinement, atomically smooth pore walls and high pore density. Our work will provide the first measurements that would compare to and hopefully validate the simulations. Gas flux is predicted to be >1000X greater for SWNTs versus zeolitesⁱ. A high flux of 6-30 H₂O/NT/ns \sim 8-40 L/min for a 1cm² membrane is also predictedⁱⁱ. Neutron diffraction measurements indicate existence of a 1D water chain within a cylindrical ice sheet inside carbon nanotubes, which is consistent with the predictions of the simulationⁱⁱⁱ.

The enabling experimental platform that we are developing is a semipermeable membrane made out of vertically aligned carbon nanotubes with gaps between nanotubes filled so that the transport occurs through the nanotubes. The major challenges of this project included:

- 1) Growth of CNTs in the suitable vertically aligned configuration, especially the single wall carbon nanotubes.
- 2) Development of a process for void-free filling gaps between CNTs
- 3) Design of the experiments that will probe the small amounts of analyte that go through

Knowledge of the behavior of water upon nanometer-scale confinement is key to understanding many biological processes. For example, the protein folding process^{iv} is believed to involve water confined in a hydrophobic environment. In transmembrane proteins such as aquaporins^v, water transport occurs under similar conditions. And in fields as far removed as oil recovery and catalysis, an understanding of the nanoscale molecular transport occurring within the nanomaterials used (e.g. zeolites) is the key to process optimization. Furthermore, advancement of many emerging nanotechnologies in chemistry and biology will undoubtedly be aided by an understanding confined water transport, particularly the details of hydrogen bonding and solvation that become crucial on this length scale. We can envision several practical applications for our devices, including desalination, gas separations, dialysis, and semipermeable fabrics for protection against CW agents etc. The single wall carbon nanotube membranes will be the key platform for applications because they will allow high transport rates of small molecules such as water and eliminate solvated ions or CW agents.

SUMMARY OF THE ACCOMPLISHMENTS

Detailed description of our accomplishments is provided in the attached manuscript, with the most recent one (submitted) containing the latest results (2). The other three publications describe the fabrication process that we developed.

- 1) We have developed a fabrication process for membranes that have carbon nanotubes as pores
- 2) We have fabricated membranes with both multiwall and double wall carbon nanotubes with pore sizes of 6-7nm and <2nm respectively
- 3) We have performed extensive characterization of these membranes through size exclusion measurements and electron microscopy and determined that less than 0.1% of the water flow goes through the pores larger than 2nm (in the double wall nanotube membrane case).
- 4) We have measured both gas and water transport through these membranes. The measured gas flow exceeds predictions of the Knudsen diffusion model by at least an order of magnitude. The measured water flow rate exceeds values calculated from continuum hydrodynamics models by two to three orders of magnitude and agrees with flow rates extrapolated from molecular dynamics simulations. The gas and water permeabilities of these nanotube-based membranes are orders of magnitude higher than those of commercial polycarbonate membranes, despite having an order of magnitude smaller pore sizes.

STRATEGIC ALIGNMENT

This project is aligned with CMS Strategic Plan in the area of the development of science on the intersection between biology, chemistry and materials science.

EXIT PLAN

This work enables further experimental study in the field of nanofluidics and at the same time has potential for various practical applications. We have prepared a proposal for BES to continue addressing the fundamental science investigations enabled by this project. The potential for high permeability with high selectivity, makes these membranes highly desirable for practical applications in water desalination and demineralization, dialysis, carbon dioxide sequestration etc. with target agencies such as DARPA, DHS, NIH. Our group has successfully won a DARPA grant to pursue CNT-based separation-science, under the DARPA micro Gas Analyzers program. The project is based on the capture of gas reagents on the outside of CNTs, rather than permeation through the middle of the tubes, but it leverages the capabilities developed by this LDRD very effectively.

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